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Base catalysis on microporous and mesoporous materials: recent progress and perspectives

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Abstract

During the past decade, new classes of porous solid bases such as organic bases grafted onto the walls of ordered mesoporous materials and nitrided zeolites have been studied as catalysts in a wide variety of base-catalyzed reactions. Important examples are the mercaptane oxidation in petroleum refining, well known as sweetening of gasoline and kerosene, carbon–carbon bond forming reactions in fine chemistry such as aldol additions and condensations, and (*trans*-) esterification reactions interesting for food, pharmaceutical and cosmetic industries. The present work gives a survey on these new solid bases, their applications in heterogeneous catalysis and on new spectroscopic techniques allowing a more detailed investigation of base sites and adsorbates on working catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Basic zeolites; Heterogeneous catalysis; Spectroscopic characterization; Test reactions

1. Introduction

In comparison to the broad application of acidic zeolites as solid catalysts in chemical technology, much less attention has been paid to basic microporous and mesoporous materials, even though these solids do have a considerable potential for a number of industrially important reactions [1]. Analyzing the industrial application of solid acid and base catalysts showed that in only 8% of the processes solid bases are being employed, and none of these reactions is performed with basic zeolite catalysts [2]. It is only with a growing effort in the preparation, characterization and catalytic investigation of new microporous and mesoporous materials with basic properties, that a breakthrough in their application may be achieved. The state of the art of basic catalysts up to the mid of the 1990s has been presented in the excellent reviews by Hattori [3] and Barthomeuf [4] which also contributed to a much better understanding of the "basicity" of zeolitic materials. It is the intention of the present paper to give a survey of basic microporous and mesoporous materials which emerged recently, to discuss new analytical methods for their characterization and to present catalytic applications which have surfaced recently.

2. Development of new basic catalysts

At the beginning of the 1990s, zeolites were used as base catalysts in their ion-exchanged and

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impregnated forms. Ion-exchanged zeolites possess only base sites of low strength, which limits their applicability in organic syntheses. They can, however, be handled in air, since their base sites are resistant to poisoning by water or carbon dioxide [3]. In order to create stronger base sites in the cavities of zeolites, impregnation with various alkali salts was carried out. Impregnation of zeolite Y with NaN_3 followed by controlled thermal decomposition yields tetrahedral Na_4^{3+} clusters in the sodalite cages, Na_y^0 clusters in the supercages and metallic clusters on the external surface [5]. In olefin isomerization, side chain alkylation of toluene and aldol condensations, a correlation between the concentration of the Na_y^0 clusters in the supercages and the catalytic activity was observed. However, the materials are sensible towards contact with air or water, which limits their utilization in catalysis. In a different approach, Hathaway and Davis formed intrazeolitic alkali oxide clusters by impregnation methods [6]. The base sites of the guest oxides were shown to be stronger than those of the zeolitic framework.

In 1995, Hattori pointed out that, for enhancing the potential of basic zeolites, further development of new preparative methods is required [3]. In the meantime, Ono and Baba found a new way of modifying zeolites to obtain basic materials [7]: Alkali-exchanged zeolite Y was immersed in a solution of metallic Na, Yb or Eu in liquid ammonia, and the solvent was removed by evacuation. Heating in vacuum at suitable temperatures (about 450 K) yielded materials which showed catalytic activity in the double bond isomerization of but-1-ene to but-2-ene, the *cis*/*trans*-ratio of the product being around 10 (ratios above unity are indicative of a base-catalyzed pathway). From this it was concluded that base sites were created on the impregnated zeolite [7]. The catalytic activity of Yb or Eu supported on the alkali-exchanged zeolite Y strongly depended on the type of alkali cation present, the order being K > Rb > Cs > Na > Li. It increased with the amount of guest compound. For Eu/K–Y, a maximum initial rate in the olefin isomerization was observed at a Eu-loading of 8 wt.%. After being evacuated at higher temperatures (900 K), the impregnated materials developed hydrogenation activity. The influence of the evacuation temperature on the catalytic activity in the isomerization of but-1-ene and the hydrogenation of ethene is displayed in Fig. 1. The results were taken as an indication that the chemical species formed on the impregnated zeolite change at ≈500 K [7]. From a characterization of the materials by fluorescence spectroscopy and TPD it was concluded that during the impregnation, metal amides are deposited inside the zeolitic channels. At 450 K, decomposition of the amides and formation of imides according to Schemes 1a and b were assumed to take place, and the imides were identified as active species for the base-catalyzed isomerization. After evacuation at higher temperatures, further decomposition to nitrides and metal-like species occurred as shown in Schemes

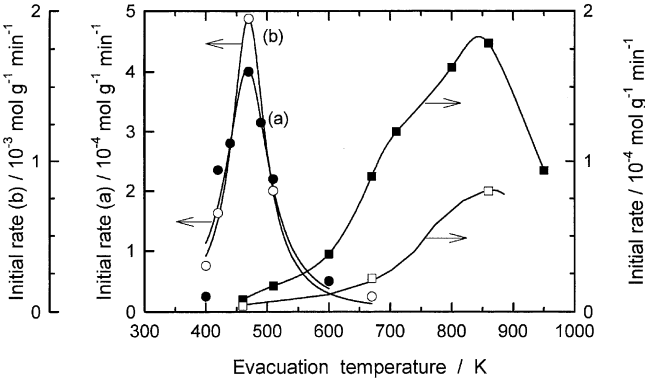


Fig. 1. Influence of the evacuation temperature on the catalytic activity for the isomerization of but-1-ene on zeolites Yb/Na–Y (•) and Eu/K–Y (○) and for the hydrogenation of ethene on zeolites Yb/Na–Y (■) and Eu/K–Y (□), after Ref. [7].

$$M(NH_2)_2 \longrightarrow MNH + NH_3, \text{ with } M = Eu, Yb \quad (a)$$

$$Yb(NH_2)_3 \longrightarrow YbNH + NH_3 + 1/2\ N_2 + H_2 \quad (b)$$

Scheme 1.

$$2\ EuNH \longrightarrow 2\ EuN + H_2 \quad (a)$$

$$EuN \longrightarrow EuN_{(1-x)} + x/2\ N_2 \quad (b)$$

Scheme 2.

2a and b. The nature of the species formed was confirmed by infrared spectroscopy, XPS and XANES [8]. EXAFS investigations on Yb/K–Y revealed that the local structures of the Yb species change drastically upon evacuation at around 500 K, viz. from a highly dispersed state to aggregated particles [9]. In summary, following this new preparation method, base sites can be created inside the pores of zeolite Y. Ono and Baba, however, also found that γ-Al_2O_3 is a better support for the amide/imide species, if strong base sites are to be formed. Impregnated γ-Al_2O_3 displayed a far higher catalytic activity in the double bond isomerization of 2,3-dimethylbut-1-ene and olefinic amines than impregnated zeolite Y [10].

Like the metallic sodium clusters in zeolite Y, the amide-impregnated materials are sensitive to contact with air or moisture, hence these materials have to be handled in an inert atmosphere. In contrast to this, Foley and coworkers claimed that cesium deposited on nanoporous carbon (NPC) is not pyrophoric [11–13]. They prepared NPC pyrolytically from poly(furfuryl alcohol)-poly(ethylene glycol) mixtures. The thus prepared material contained nanopores with sizes distributed around 0.5 nm and larger pores with sizes around 10 nm which allowed access to catalytic sites situated in the nanopores [12]. Cesium vapors were rapidly and strongly adsorbed onto the NPC. Cesium was chosen as the most electropositive element and because its covalent atomic diameter is close to the nanopore size of the NPC. A cesium content of up to 42 wt.% could be achieved, and Cs was reported to be finely dispersed in the porous system. Magnetic susceptibility and EPR measurements indicated that electrons of Cs were donated to the carbon [11]. Cs/NPC was active in the isomerization of but-1-ene, yielding a *cis*/*trans*-ratio of the but-2-ene formed up to 9. Upon evacuation at temperatures up to 773 K, no desorption of Cs was observed, whereas intercalated Cs/graphite compounds exfoliated under these conditions. After contacting Cs/NPC to air, an X-ray diffraction pattern with sharp lines was observed, which did not match any of the known cesium hydroxides or oxides [13]. Therefore, the formation of an intermediate hydrous oxide structure was assumed. Samples conventionally impregnated with CsOH solution showed XRD patterns indicating the presence of large hydroxide crystals. When the two types of materials were used as catalysts in the vapor phase aldol condensation of acetone, both a higher activity and a higher isophorone selectivity were achieved with the oxidized Cs/NPC. From this it was concluded that, by depositing Cs on NPC followed by oxidation in air, a finely dispersed hydrous oxide species is formed which may be used as an active base catalyst [13].

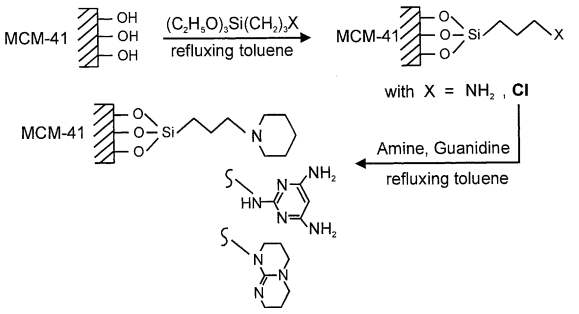
In the 1990s, another kind of solid base catalysts with high specific surface area was developed, which contains nitrogen rather than oxygen atoms as basic sites. Treating amorphous aluminum orthophosphate [14–18], zirconium phosphate [19], aluminum vanadate [20,21] or galloaluminophosphate [22] with ammonia at temperatures of 973–1273 K, the oxygen is replaced by nitrogen in a three-step process: First, ammonia is adsorbed on Brønsted or Lewis acid sites of the oxide surface. In a second step, surface hydroxyl groups are replaced by amino groups, and water is desorbed [19,23]. In phosphorus containing oxides, P–O-bonds are cleaved preferentially [14,18,23]. Condensation of the amino groups with further hydroxyl groups yields imides and nitrides. The incorporation of nitrogen into the bulk phase occurs by diffusion. The amorphous oxynitrides are active in base-catalyzed reactions. They are considered to be more strongly basic than alkali ion-exchanged zeolites and comparable to hydrotalcites or MgO [24]. The nature of the base sites is, however, still under discussion. Among the species proposed are terminal NH_2 and bridging NH groups as well as N^{3-} [17–19,25], deprotonated hydroxyl groups with adsorbed ammonium ions

[21,22] and double bonded oxygen atoms formed during the incorporation of nitrogen [19]. Crystalline materials do not react as easily with ammonia as the amorphous oxides. After high-temperature (>1073 K) treatment of $AlPO_4$-5 with ammonia, the formation of P–NH_2 groups was observed, but no Al–N bonds or P–NH–Al bridging groups appeared. Only part of the oxygen was replaced by nitrogen [26]. The reaction of NH_3 with the aluminophosphate framework was considered analogous to steaming with water, leading to the creation of amino nests. Likewise, treatment of zeolite H–Y with ammonia at 773 K led to the formation of terminal NH_2 groups only [27]. Zeolite Na–Y ammonia-treated at 1073 K did not show catalytic activity in the Knoevenagel condensation of benzaldehyde and malononitrile. After heating the zeolite in a stream of ammonia at 1123 K or 1148 K for 20–72 h, active catalysts for the condensation reaction were obtained [28]. The structural integrity of the zeolite samples was retained after nitridation. The chemical nature of the basic sites generated remains to be clarified.

One reason for the limited application of zeolite catalysts in the synthesis of fine chemicals resides in their small pore openings which prevent bulky molecules from reaching the active sites. As a logical remedy, the use of mesoporous materials MCM-41 as carriers for basic guest species has been proposed [29,30]. By impregnation of MCM-41 with cesium acetate in aqueous or methanolic solution and subsequent calcination, finely dispersed cesium oxide clusters were obtained in the pores of the carrier, as long as the cesium content did not exceed 10 wt.%. From CO_2-TPD measurements it was concluded that larger, aggregated oxide clusters form at higher cesium loadings [30]. The BET surface area and the pore volume of the parent MCM-41 decreased after impregnation, which was attributed to the presence of the guest oxides and eventual pore blocking rather than to a destruction of the regular pore structure. The impregnated MCM-41 material was active in typically base-catalyzed reactions like Knoevenagel condensations or Michael additions. In the reaction of diethyl malonate with neopentyl glycol diacrylate, shape selectivity was observed: While on bulk cesium oxide, the addition of diethyl malonate to both double bonds of neopentyl glycol diacrylate occurred, only the mono-adduct was formed on CsO_y/MCM-41 due to steric restrictions [30]. However, the impregnated material did not show a good thermal and chemical stability. After repeated calcination or after the use as catalyst, aggregation of the cesium oxide particles and a significant reduction of the specific surface area were observed. The latter was explained by a reaction of cesium oxide with the MCM-41 material, possibly forming a cesium silicate species [30,31]. More stable materials were obtained by impregnating MCM-41 simultaneously with cesium acetate and lanthanum nitrate [31,32]. In this case, a $CsLaO_x$ guest compound was formed in the channels of MCM-41, the base strength of which was, however, lower than that of the CsO_y guest oxide. From ^{133}Cs MAS NMR spectroscopic measurements it was deduced that the mixed oxide is bound to the carrier via La–O bonds. No interaction of cesium with MCM-41 was found. This was interpreted as a possible reason for the improved stability of $CsLaO_x$/MCM-41 [31]. This material is not moisture-sensitive, it can even be used for catalyzing Knoevenagel condensations in aqueous media [31].

Recently, a new way of modifying MCM-41 has been described: The material was functionalized by anchoring organic bases at the silanol groups. By forming a covalent bond between the inorganic host and the organic guest species, a higher stability against leaching was aimed at [33]. On the basis of reports on the basicity of amino-functionalized silica gel [34], Chauvel and coworkers developed procedures for anchoring primary and tertiary amines at the silanol groups of MCM-41 [33,35]. By reacting MCM-41 with 3-chloropropyltriethoxysilane and piperidine, pyrrolidine, pyrimidine or triazabicyclo[4,4,0]dec-5-ene in subsequent steps, various organic bases could be bound to the surface of MCM-41 [33,35–39]. Some examples are shown in Scheme 3.

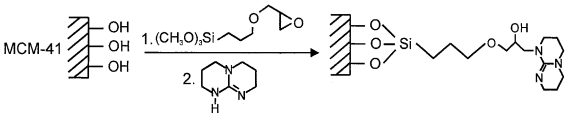
Subba Rao et al. proposed a different agent for linking the organic base to the inorganic carrier [40]. They pointed out that the route described above will lead to immediate poisoning of the strongest base sites due to HCl liberated in the synthesis. This was proven by Jaenicke et al. who



Scheme 3.

found by potentiometric titration that 30–40% of the potential base sites are indeed blocked by HCl [38]. To avoid this problem, 3-methoxysilylpropoxymethyloxirane with a glycidyl group as the binding site can be used in the anchoring reaction, as shown in Scheme 4. Other groups varied the synthesis conditions (Scheme 5): By reacting the silanol groups of MCM-41 with 3-trimethoxysilylpropyl(trimethyl)ammonium chloride and subsequently exchanging the chloride by hydroxide ions, materials with free OH^- ions were obtained [41,42]. A method for directly preparing aminopropylated MCM-41 in a one-step synthesis has also been described [43–45].

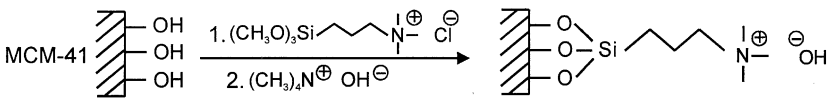
The organic–inorganic hybrid materials are less strongly basic than the corresponding free organic molecules and possess a wide distribution of base sites with different strengths, which has been explained by an H-bonding interaction of the amine function with residual silanol groups [37,38,41]. They nevertheless catalyze Knoevenagel condensations and Michael additions under mild reaction conditions [33,40–42]. While organo-functionalized MCM-41 materials are truly fascinating, they possess two drawbacks which could hamper their widespread use as catalysts: (i) Their preparation is rather complicated and expensive and (ii) they can only be applied at temperatures lower than ≈170°C, at higher temperatures degradation of the organic molecules occurs [38]. This also rules out, a reactivation of the spent catalysts at elevated temperatures.



Scheme 4.

The incorporation of an organic base into the pores of zeolite Y has been attempted by using the "ship-in-the-bottle" synthesis method [46]. By reacting *N*,*N*′-dicyclohexylcarbodiimide with cyclohexylamine in the supercages of dealuminated zeolite Y, encapsulated *N*,*N*′,*N*″-tricyclohexylguanidine was formed, which is displayed in Fig. 2. The product molecule is too large to diffuse out of the cages. The thus obtained host–guest compound was, however, only weakly basic.

While for some applications strongly basic materials are sought, in other reactions catalysts possessing base sites of medium strength or even a combination of mildly basic and acidic sites appear to be preferable [47]. In this context, hydrotalcite-derived base catalysts, known since the 1980s [48], continue to attract research interest. Hydrotalcite is a clay mineral which can be synthetically prepared. The structure of hydrotalcite is formed by brucite-like Mg–Al–hydroxide layers and intercalated CO_3^{2-} and OH^- anions. Calcination of hydrotalcite leads to dehydroxylation of vicinal hydroxyl groups in the brucite layers and decarboxylation of the carbonate ions, accompanied by desorption of water and carbon dioxide. A porous mixed oxide remains which possesses a higher specific surface area than the hydrotalcite [49]. As long as the calcination temperature does not exceed 773 K, the decomposition of the hydrotalcite structure is reversible. The mixed oxide was more



Scheme 5.

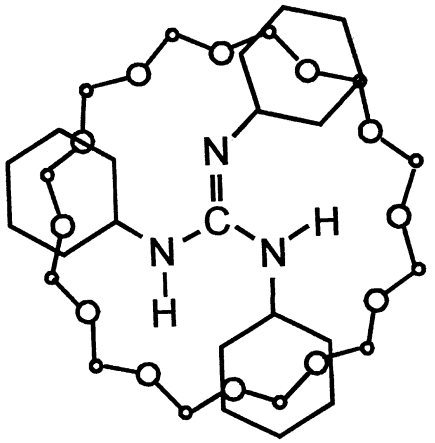


Fig. 2. Zeolite-encapsulated *N*,*N*′,*N*″-tricyclohexylguanidine, after Ref. [46].

active in Knoevenagel condensations than ion-exchanged zeolites, but its base sites appear to be weaker than those of pure MgO [50,51]. Surface hydroxyl groups and more strongly basic O^{2-} ions have been identified as active sites of the calcined hydrotalcite. Recently, a deliberate rehydration of the mixed oxide was reported to yield a base catalyst with free OH^- ions [52,53]. The base strength of the rehydrated surface was shown to be lower in comparison to the mixed oxide, however, the rehydrated sample was more active in the aldol condensation of benzaldehyde and acetone. Therefore it was concluded that the aldolization reaction is catalyzed by hydroxide ions [53].

3. Modern methods for the characterization of basic zeolites

Suitable methods for the direct investigation of basic oxygens in zeolitic materials are X-ray photoelectron spectroscopy (XPS) and ^{17}O NMR spectroscopy. With XPS the binding energies of O_{1s} electrons are evaluated which could be shown to correlate with the base strength of framework oxygens in zeolites [54,55]. During the last years the introduction of superconducting magnets with magnetic fields of up to 18.8 T and new techniques of high-resolution solid-state NMR spectroscopy opened new possibilities of investigating ^{17}O nuclei in solid materials [56]. High magnetic fields, double oriented rotation (DOR) of powder samples and two-dimensional multiple-quantum MAS spectroscopy (MQMAS) overcome the problems of strong signal broadening by the second-order quadrupolar interaction of ^{17}O nuclei having a nuclear spin of $I = 5/2$ [56,57]. For low-silica faujasites with a framework n_{Si}/n_{Al} ratio of 1 (LSX) which contain Si–O–Al bridges only, the spectra show four lines due to oxygen atoms at the four different crystallographic positions. For oxygens at O-1 sites in zeolite LSX a correlation was found between the ^{17}O chemical shift, δ_{17O} and the cation radius, r, in the hydrated zeolites Li–LSX, Na–LSX and Cs–LSX: $\delta_{17O} = 9.2\ r(\text{Å}) + 41.47$ [58]. This indicates that the framework oxygens in zeolites LSX are affected by the introduction of different alkali cations. Quantum chemical simulations will have to clarify whether this variation of the ^{17}O chemical shift indicates a change in the base strength of the corresponding framework oxygens or whether it is due to a variation of the T–O–T bond angles. The investigation of zeolites with $n_{Si}/n_{Al} > 1$ requires a further improvement of the NMR spectroscopic techniques since the presence of Si–O–Al and Si–O–Si bridges leads to a superposition of at least eight signals which are, in addition, broadened by a distribution of chemical shifts.

Up till now, the most widely applied technique for the investigation of base sites on solid catalysts is the application of molecular probes and their study by temperature-programmed desorption experiments (TPD), FTIR spectroscopy, X-ray photoelectron spectroscopy and NMR spectroscopy [4,59,60]. A frequently used molecular probe is carbon dioxide. The adsorption of this probe on alkali-exchanged zeolites, however, is not as straightforward as one might be tempted to assume: Different adsorbate structures may form, and on strongly basic guest compounds surface carbonates can occur [60]. Both these effects complicate the TPD curves and FTIR spectra of CO_2 on basic zeolites [61]. A recent review by Knözinger and Huber [59] gives a survey of the application of pyrrole, acetylenes and deuterated chloroform as FTIR probes for the investigation of basic solids. The spectra obtained with these

probes tend to be less complicated than those observed with CO_2, but the occurrence of different adsorption structures may again render the interpretation difficult. For alkali-exchanged zeolites, good correlations have been found between the shift of the stretching frequency and the electronegativity of the exchanged cation. The main drawback of C–H and N–H acids used as probe molecules is the possible dissociation of the C–H or N–H bond on strongly basic surface sites. As this leads to a disappearance of the analytical signal, those strong base sites may not be detected by the probe molecules.

Very recently, Sánchez–Sánchez et al. applied pyrrole and chloroform as NMR probes for basic zeolites [62,63]. Fig. 3 shows ^{1}H MAS NMR spectra of pyrrole adsorbed on various alkali-exchanged zeolites Y and X [62]. The hydrogen atoms at the rings of the pyrrole molecules are not influenced by the different zeolites and cause the two signals at 6–7 ppm. The ^{1}H NMR shift of the hydrogen atoms at the ring nitrogens, however, covers a range between 8.4 and 11.5 ppm and indicates the different base strengths of zeolite oxygen atoms contributing to the H-bondings with the pyrrole molecules. An important advantage of the NMR probe pyrrole is the remarkable sensitivity (large shift range) and the good resolution of the MAS NMR spectra.

Independently of the spectroscopic method applied, an important disadvantage of the above-mentioned probe molecules are the facts that most of them are not totally unreactive in the presence of strong base sites and that they form different adsorption structures complicating an evaluation of the spectra. An interesting technique which seems to be free from these problems is the use of methoxy groups directly formed at the basic framework oxygens by a conversion of methyl iodide, as spectroscopic probes. Applying ^{13}C MAS NMR spectroscopy, Bosacek and coworkers [64,65] found a correlation between the isotropic chemical shift of these surface methoxy groups bound to zeolite oxygens in bridging positions and the mean Sanderson electronegativity, S, of the zeolite framework (see Fig. 4). According to this correlation, a low ^{13}C NMR shift of methoxy groups corresponds to a high base strength of the framework oxygen atoms. Methoxy groups bound at framework oxygens of alkali-exchanged zeolites Y and X cover a range of ^{13}C NMR shifts from 54.0 to 56.5 ppm. For zeolites Y and X impregnated with basic guest compounds such as alkali

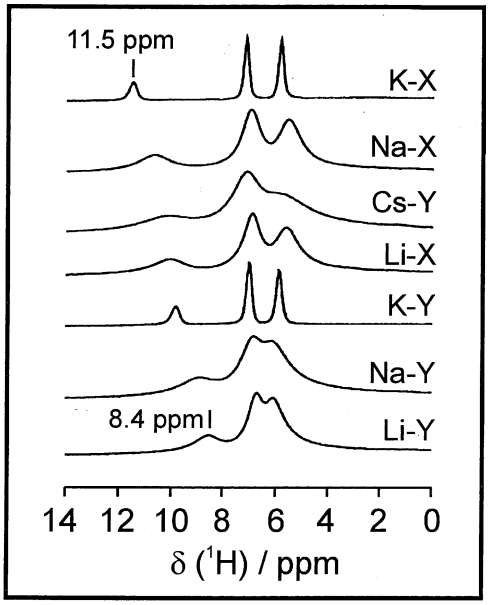


Fig. 3. ^{1}H MAS NMR spectra of pyrrole adsorbed on various alkali-exchanged zeolites Y and X, after Ref. [62].

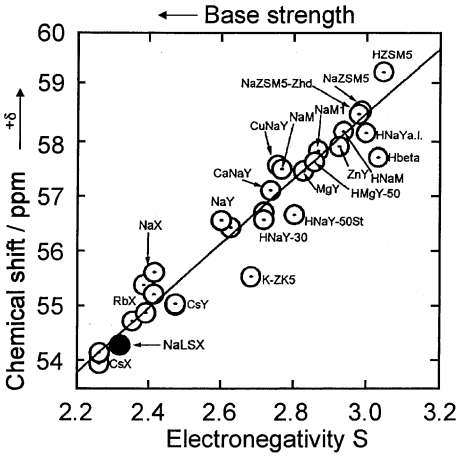
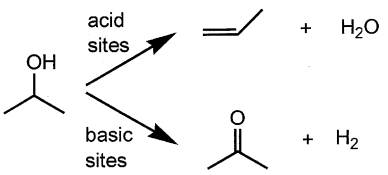


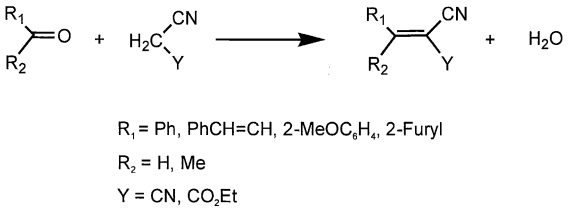
Fig. 4. Dependence of the ^{13}C MAS NMR shift of methoxy groups bound on framework oxygens in bridging positions on the mean Sanderson electronegativity, S, of the zeolite frameworks, after Ref. [65].

oxides, additional signals of methoxy groups occur at 50 ppm. Since a stepwise increase of the methyl iodide adsorption on zeolites Y and X impregnated with alkali oxides leads to a preferential formation of methoxy groups at 50 ppm, a signal at this resonance position indicates the presence of a strongly basic compound. In a recently published work, for zeolites Y and X impregnated with alkali metal hydroxides, two high-field signals of methoxy groups bound at strongly basic guest compounds were found at 50.0 and 52.3 ppm [66]. According to Krawietz et al. [67], guest compounds formed by impregnating a support with cesium hydroxide or acetate are a mixture of cesium oxide (Cs_2O), peroxide (Cs_2O_2) and superoxide (CsO_2). The ^{13}C NMR signals observed at $\approx$50 and 52 ppm could, therefore, be a hint at the presence of different basic guest compounds on impregnated zeolites Y and X.

A very popular technique for characterizing basic solids is the application of catalytic test reactions. The selectivities of several reactions give evidence for the presence of base sites with different strengths. In a recently published paper, Aramendia et al. [68] compared the transformation of 1-phenylethanol, 2-propanol and 2-methyl-3-butyn-2-ol on basic catalysts (Scheme 6). The authors were able to show that some of these alcohols (in particular 1-phenyl ethanol and 2-propanol) can undergo both dehydrogenation and dehydration on basic sites, hence no unambiguous conclusions concerning the nature of the active sites can be drawn from the measured selectivities. On the other hand, in agreement with Handa et al. [69], it was found that selectivities in the decomposition of 2-methyl-3-butyn-2-ol do allow a discrimination between acidic and basic catalysts. A further test reaction which finds increasing application is the Knoevenagel condensation (Scheme 7) [70–73]. An



Scheme 6.

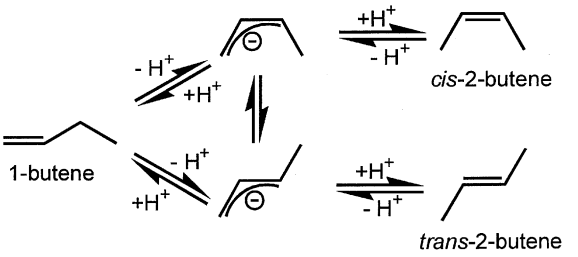


R_1 = Ph, PhCH=CH, 2-$MeOC_6H_4$, 2-Furyl

R_2 = H, Me

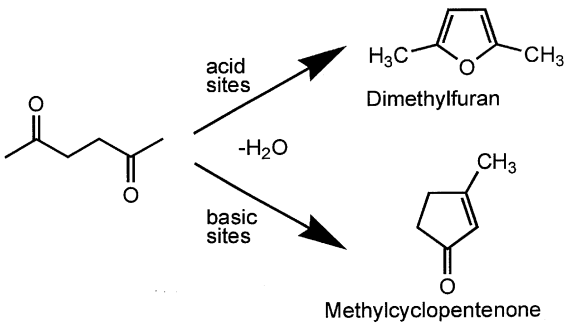
Y = CN, CO_2Et

Scheme 7.



Scheme 8.

important advantage of this liquid-phase reaction is that it can be performed with reactants having different acidities. However, problems with diffusional hindrance in microporous catalysts limit its application for the characterization of basic zeolites. Double bond isomerization of 1-butene and 2,3-dimethylbut-1-ene leading to 2-butene and 2,3-dimethylbut-2-ene, respectively, is useful for the characterization of strong solid bases at low temperatures (Scheme 8) [69,74,11]. In the case of the isomerization of 1-butene, the *cis*/*trans* ratio of the 2-butenes gives a measure of the base strength. While the isomerization is a useful test reaction for determining the relative activities of strong solid bases, only very little or no conversion at all was found for alkali-exchanged zeolites [69]. Two decades ago, Dessau introduced the dehydration of acetonylacetone as catalytic test reaction (Scheme 9) [75]. Under specified conditions, the ratio of the selectivities of methylcyclopentenone and dimethylfuran (S_{MCP}/S_{DMF}) is usually taken as a measure for basicity. Recently, Alcaraz et al. showed that the dehydration of acetonylacetone allows the catalytic characterization of materials exhibiting acidic as well as basic sites over a broad range of acid and base strengths [76].



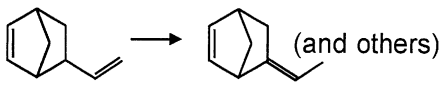
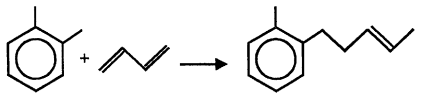
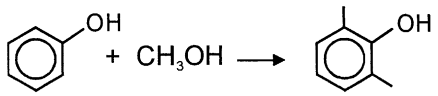
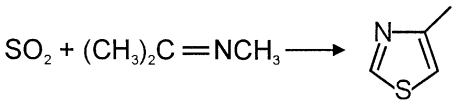
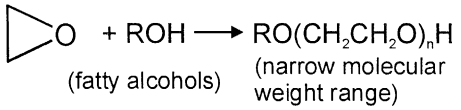
Scheme 9.

4. Applications of solid base catalysts

The application of solid base catalysts in industrial processes is rather limited: Out of 127 processes which make use of acid or base catalysts, only 10 are catalyzed by bases [2]. Examples are shown in Table 1. Only one of the processes (No. 5 in Table 1), being in a pilot plant stage, uses a zeolitic catalyst [2]. However, a lot of effort has recently been directed towards investigations concerning catalytic applications of solid bases, including basic zeolites. Some examples which, in the authors' opinion, deserve particular attention will be discussed in this paragraph.

Most studies concerning the use solid base catalysts are related to fine chemicals production. One exception is the use of a hydrotalcite-derived catalyst for mercaptane oxidation in petroleum refining [76]. In this so-called sweetening of gasoline and kerosene, aqueous alkaline solutions (caustic) are used as co-catalysts in the conversion

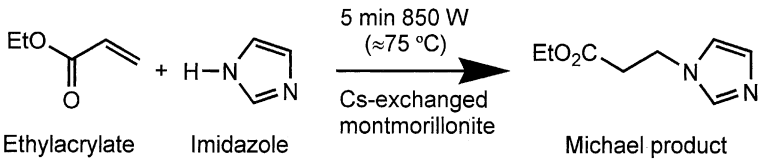
Table 1
Some industrial processes catalyzed by solid bases, after Ref. [2]

Process		Catalyst	Company
1		$Na/NaOH/\gamma\text{-}Al_2O_3$	Sumitomo Chemical 1986, 2000 t/a
2		Na/K_2CO_3	AMOCO Chemical 1995, 45 000 t/a
3		MgO	General Electric, BASF
4	*n*-Alcohols + $H_2S \rightarrow$ Mercaptanes	Alkali oxides/ Al_2O_3	Elf-Atochem 1000–30 000 t/a
5		Cs_2SO_4/ZSM-5	Merck, pilot plant
6		Hydrotalcite	Henkel, pilot plant

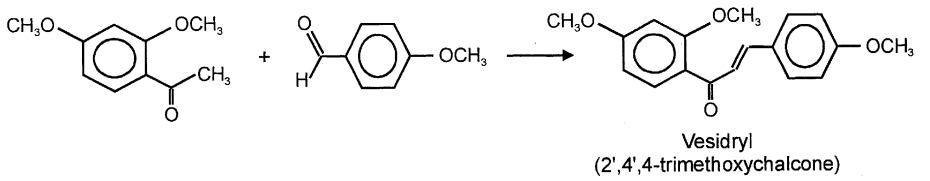
of mercaptanes to disulfides in the presence of a transition metal compound (typically sulfonated cobalt phthalocyanine). The problem associated with the use of caustic arises from the fact that caustic is not converted into a valuable product, but must be discarded at high costs [76]. This can be overcome if the liquid base is replaced by a layered double hydroxide (hydrotalcite) calcined at ≈450°C and impregnated with a solution of sulfonated cobalt phthalocyanine in methanol. In gasoline sweetening, mercaptane conversions into disulfides >99% were achieved and, since gasoline feeds are relatively clean, no catalyst deactivation was observed. By contrast, rapid deactivation occurred in kerosene sweetening due to (i) rehydration of the calcined basic oxide to hydrotalcite, (ii) poisoning of the basic sites by naphthenic acid impurities and (iii) strong adsorption of heavy and polar hydrocarbons. These problems were solved by adding nickel to the catalyst formulation, thus obtaining a catalyst which does not rehydrate, by removing the acid species present in the kerosene prior to sweetening and by adding a surfactant to prevent the build-up of heavy hydrocarbon species on the catalyst surface [76].

In the field of fine chemistry, important steps in the synthesis of relatively large and complex molecules include carbon–carbon bond forming reactions such as aldol additions and condensations, Knoevenagel condensations or Michael additions. Replacing the conventional liquid base catalysts, mostly solutions of alkali metal hydroxides and alkoxides, by solids can be desirable for various reasons, e.g., to suppress undesired side reactions (polymerization, self-condensation) or to avoid salt formation due to the necessary neutralization of the soluble bases. In this context, it has been shown that in Knoevenagel condensations and Michael additions of various components high product yields can be obtained under mild reaction conditions and in short reaction times using calcined and rehydrated hydrotalcite [52]. Zeolite X containing metallic sodium clusters and cesium oxide as guest components were applied in the Michael addition of ethyl acrylate and acetone forming 5-oxohexanoic acid ethyl ester [77]. Such esters can be ring transformed and dehydrogenated to resorcines which are valuable components for the production of rubber materials. Conversions around 50–80% and selectivities around 60–70% were achieved, and the cesium oxide containing catalyst proved to be reusable. However, the results were not as good as those obtained in homogeneous systems [77]. Using a basic clay (Cs-exchanged montmorillonite), Martín-Aranda et al. conducted the Michael addition of ethyl acrylate and imidazole in a microwave oven (Scheme 10). After 5 min of irradiation (850 W), 75% conversion were observed [78]. The Michael product is a model compound for guanine- and adenine-based anti-viral compounds, e.g., acyclovir, pencyclovir or famcyclovir. Knoevenagel condensations of malononitrile with cyclohexanone, benzophenone and *p*-amino acetophenone yield alkenes containing electron withdrawing nitrile groups, which facilitate additions to the double bond. These alkenes are useful in anionic polymerization reactions leading to plastics, synthetic fibers or the production of liquid crystals. They can be synthesized using ion-exchanged zeolite X, sepiolite and hydrotalcite as catalysts [79].

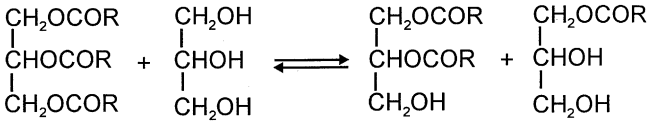
In an aldol condensation between a ketone, acting as methylenic compound, and an aldehyde (Claisen–Schmidt condensation), Vesidryl has been formed from substituted acetephenone and substituted benzaldehyde (Scheme 11). Vesidryl is a pharmacologically interesting product due to its diuretic and choleretic properties. By use of calcined hydrotalcite as a catalyst (5 wt.%), after a reaction time of 20 h at 170°C an 85% yield of



Scheme 10.



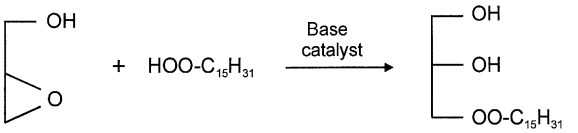
Scheme 11.



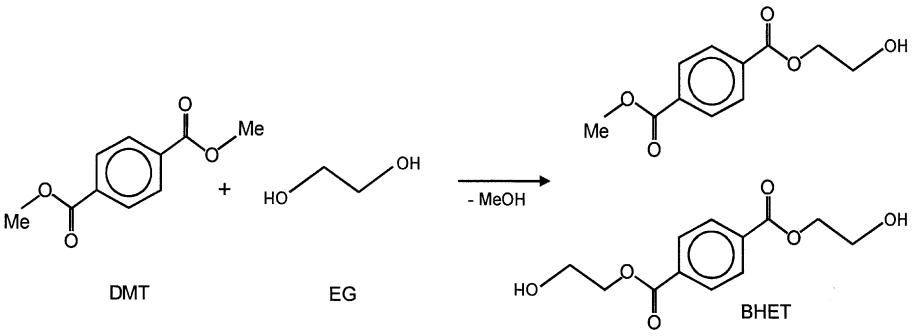
Scheme 12.

Vesidryl has been achieved [80]. Catalyst deactivation was observed in this reaction and was explained by oxidation of the aldehyde forming the acid which poisons the base sites. Reactivation of the catalyst was achieved by calcination at 450°C for 3 h.

A further application of base catalysts are (*trans*-) esterification reactions. By reaction of rapeseed oil with an excess of glycerol, as shown in Scheme 12, mono- and diglycerides are formed which are important emulsifiers used in the food, pharmaceutical and cosmetic industries. Industrial glycerolysis is carried out at temperatures above 200°C with NaOH, KOH or hydrated lime, $Ca(OH)_2$, as catalysts. After completion of the reaction, the catalyst has to be neutralized to prevent the reversion of the reaction and to avoid a soapy taste, unstable color or foaming of the final products. Subsequently, the products are filtered by clays, where a part of the monoglycerides remains irreversibly adsorbed. To overcome these disadvantages, the use of ion-exchanged sepiolite and MCM-41, MgO and calcined hydrotalcite as catalysts has been proposed [81]. With MgO or calcined hydrotalcite, >95% conversion of rapeseed oil and 75% selectivity towards the monoglyceride are achieved after 5 h reaction at 240°C. The catalyst can be filtered off, and the product obtained after extraction in hexane and evaporation of the solvent meets European quality standards [81]. Monoglycerides can alternatively be prepared by direct esterification of fatty acids with glycidol, as shown in Scheme 13. MCM-41 functionalized with organic bases has been tested in the esterification of lauric acid with glycidol [35,37,38]. With MCM-41 containing aminopropyl groups, 15% yield of the monoglyceride were observed after 6 h of reaction. Tertiary amino groups proved to be more active, a yield of 59% was achieved in the presence of grafted piperidine. The selectivity could be improved by treating the grafted catalysts with hexamethyldisilazane vapor, thereby masking residual silanol groups of the MCM-41 material which undergo side reactions with glycidol [35]. A similar improvement of selectivity was observed when the catalyst was re-used a second time. It was found that spent catalysts can be re-used in the reaction without intermediate treatment. When guanidine base-grafted MCM-41 was used in a second run, the monoglyceride was formed with 58% yield after a reaction time of 2 h and with 95% yield after 24 h [37]. This catalyst could be re-used for 11 cycles with a duration of 2 h and showed very little loss of activity [38]. The transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) yields bis(2-hydroxyethyl) terephthalate (BHET, Scheme 14) which is important as a monomer for the production of polyethyleneterephthalate



Scheme 13.



Scheme 14.

(PET). Using zeolite Na–X in the transesterification reaction at 180°C (molar ratio of DMT/EG = 1:5), Meyer et al. observed an almost complete conversion of DMT after 6 h of reaction, however, only one ester group of DMT reacted [82]. With cesium oxide-impregnated zeolite X, 94% conversion were achieved after 6 h, and the bis-product was formed with a selectivity of 59%. The rather low selectivity was caused by undesired oligomerization and polymerization reactions. Di-methyl carbonate can also be prepared in a transesterification reaction, using EG and methanol as reactants [83]. This reaction has been proposed as one possible non-phosgene route to dimethyl carbonate which has received renewed attention as a potential octane enhancer in gasoline, as a precursor of polycarbonate resins and as a methylating agent. With hydrotalcite catalysts, 70% ethylene carbonate conversion and 58% yield of dimethyl carbonate can be achieved in a batch reaction ($n_{\text{methanol}}/n_{\text{ethylene carbonate}} = 4$, $m_{\text{methanol+ethylene carbonate}}/m_{\text{cat.}} = 75$, reaction time = 3 h) [83]. Interestingly, the as-synthesized hydrotalcite displayed a higher catalytic activity than the calcined material. The catalytic activity increased with increasing Mg content of the hydrotalcite samples. This result was attributed to a growing number of weak base sites [83]. A number of different transesterification reactions have been carried out achieving high yields at short reaction times by use of a hydrotalcite material ion-exchanged with the *tert*-butoxide anion as catalyst [84]. The ion-exchanged hydrotalcite gave higher yields in shorter reaction times than the as-synthesized or calcined material, which was explained by the presence of stronger base sites in the ion-exchanged sample. The modified hydrotalcite was found to be re-usable in several reaction cycles.

A possible application for basic zeolite and hydrotalcite catalysts in the food industry has been described by Moreau et al. [85]. The isomerization of glucose into fructose in alkaline medium is of interest, because fructose is used as a diet sugar and as a starting material for the synthesis of furanic precursors of non-petroleum derived polymeric materials. Among different alkali ion-exchanged zeolites, Na–X and K–X presented the best balance between catalyst activity and selectivity to fructose. In a continuous experiment using 14 g of Na–X as catalyst (reaction temperature = 95°C, concentration of glucose in water = 100 g/l, flow rate = 0.15 cm^3/min), 25% glucose conversion was observed after 5 h on-stream. The conversion decreased to 10% within the next 20 h and remained stable afterwards. The catalyst deactivation was explained by leaching of alkali cations into the aqueous solution. As the process results were considered industrially interesting, the use of a binder material to suppress the dissolution phenomenon has been proposed [85].

Research is as well going on in other fields of base catalysis, such as oxidative methylation of toluene with methane on basic zeolites Ref. [86], alkylation reactions (see, for example, Refs. [87–89]) or oxidations of organic compounds. The use of basic solids in oxidation reactions, recently reviewed by Fraile et al. [90], comprises three functions: as a support for the oxidant the solid base helps to control the acidity of the oxidant (useful if

organic substances with acid-sensitive functional groups are involved), or, more importantly, they can activate either the oxidant or the substrate. Especially hydrotalcites can be employed to accommodate redox active centers by including them as part of the structure or incorporating them in between the brucite layers by ion exchange [90].

For many reactions there is a considerable incentive for replacing the traditional liquid bases by solids for at least one of the following reasons: (i) high costs of product/catalyst separation, (ii) corrosiveness and (iii) the costs associated with the disposal of spent or neutralized caustic. However, several problems are frequently encountered when solid bases are applied as catalysts: The solids are often less active than soluble bases, which may be due to transport limitations and strong reactant/product adsorption. Therefore, more drastic reaction conditions are often required than in homogeneous systems, and this can have detrimental effects on the selectivity or product stability. In industrial catalysis, deactivation is a very disturbing factor, hence more intense fundamental research concerning the deactivation mechanisms has been called for [47].

We have studied several solid base catalysts in the aldol condensation of *n*-butyraldehyde by means of in situ infrared spectroscopy in order to elucidate the reasons for the severe catalyst deactivation occurring in this reaction. In the self-condensation of *n*-butyraldehyde, 2-ethylhexenal is formed which is hydrogenated forming 2-ethylhexanol, a key intermediate in the production of ester plasticizers. The production capacity of 2-ethylhexanol amounts to over 2×10^6 t/a [91]. Solid base catalysts are initially very active in the condensation reaction, and 2-ethylhexenal is formed with a selectivity of almost 100%. Unfortunately, fast deactivation occurs, for which several explanations have been offered: (i) Side reactions occurring on Lewis acid sites of zeolite catalysts [92], (ii) the formation of oligomers which block the active sites [93] and (iii) the formation and hydrolysis of butyl butyrate which leads to poisoning of the active sites by butyric acid [94]. None of these interpretations, however, was based on direct experimental evidence. In Fig. 5, infrared spectra are displayed which have been obtained during the gas-phase aldol condensation of *n*-butyraldehyde on self-supporting zeolite wafers, carried out in a transmission cell suited for flow conditions (reaction temperature = 150°C, WHSV = 2 h^{-1}). For cesium-exchanged zeolite Y, which was not very active in the condensation reaction (initial conversion determined by on-line gaschromatography: 4%), only C=O stretching vibration bands of *n*-butyraldehyde (1704 cm^{-1}) and of 2-ethylhexenal (1657 cm^{-1}) were observed. However, for cesium-exchanged zeolite X, being initially far more active than CsNa–Y, a third band developed with increasing time-on-stream at 1580 cm^{-1}. This band can be attributed to a

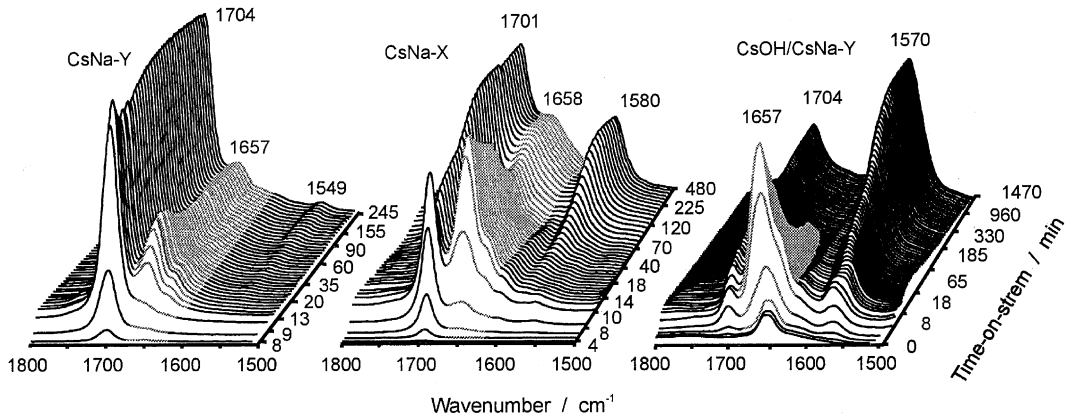


Fig. 5. Infrared spectra recorded during the aldol condensation of *n*-butyraldehyde on different zeolites.

COO^- stretching vibration of a carboxylate anion [95]. The development of this band occurs even faster and in a more pronounced manner on cesium-impregnated zeolite Y and is accompanied by a drop in the product C=O stretching band intensity and the loss of catalytic activity. It appears that a carboxylic acid is formed in a side reaction, presumably via a Tishchenko reaction forming *n*-butyl butyrate which subsequently decomposes forming butyric acid and butanol [3,94]. The acid is deprotonated at the base sites of the catalyst. The alcohol could not be detected by on-line gas-chromatography, but it was found in an integral, condensed sample of the reactor effluent. From the in situ monitoring of the adsorbates on the catalyst surface during the condensation reaction it can be concluded that catalysts possessing strong base sites do not only enhance the yield in the aldol condensation, as seen in the infrared spectra by the high intensity of the product C=O stretching vibration, but they also promote the undesired side reaction. In summary, poisoning of the active sites by a carboxylic acid appears to be the main reason for catalyst deactivation, at least for the initially very active materials. To prevent their deactivation, ways have to be found to suppress the side reaction in which the acid is formed.

5. Conclusions

In his excellent review published in 1995, Hattori [3] stated that "to reveal the potential of basic zeolites, the preparative methods have to be developed, and the identification of the basic sites and the application of basic zeolites to a wide variety of base-catalyzed reactions are required." Meanwhile, new classes of porous solid bases have emerged, e.g., organic bases grafted onto the walls of ordered mesoporous materials and nitrided zeolites, and will probably continue to emerge. It is, however, too early to fully assess their potential in applied catalysis. We perceive ongoing progress in the characterization of basic solids through spectroscopy and suitably selected test reactions, though no single technique seems to exist which is optimal for all systems.

During the past decade, catalysis on solid bases has become a rather popular field of research. In particular, the number of reaction types screened has expanded considerably. They are now covering the whole span from petroleum refining till the manufacture of highly complex molecules in fine chemistry. In situ spectroscopic techniques (IR, NMR and possibly others) are rapidly conquering heterogeneous catalysis. We anticipate that these techniques will furnish new and detailed information on the adsorbates on the working catalysts, thus helping to elucidate reaction and deactivation mechanisms.

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